Formation of unusual prenyl pyrophosphates by (SAM)-dependent methyltransferases

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Terpenoids represent the largest and most diverse class of natural products with more than 80.000 compounds.[1] Although the terpene biosynthesis pathways are highly modular and lead to immense structural diversity, their universal terpene building blocks are almost exclusively the C_5 units IPP (isopentenyl pyrophosphate) and DMAPP (dimethylallyl pyrophosphate). The structural diversity of terpenoids and thereby the biotechnological exploitation of terpenoid biosynthesis would be greatly expanded if modifications could be added to the canonical building blocks. Such a strategy would take advantage of the generally high substrate promiscuity of prenyltransferases and terpene synthases.

For this purpose, we screened bacterial genome sequences for uncharacterized prenyl pyrophosphate methyltransferases and we were able to identify S-adenosyl-L-methionine (SAM)-dependent methyltransferases which can convert prenyl pyrophosphates into a variety of methylated derivatives. Compared to the canonical building blocks these novel prenyl pyrophosphates have additional methyl groups.

(1) D. W. Christianson, *Chem. Rev.* 2017, 117, 11570